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Detection of H₂S, SO₂ and NO₂ in CO₂ at pressures ranging from 1-40 bar by using broadband absorption spectroscopy in the UV/VIS range

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Abstract

This paper presents a methodology to quantitatively measure H₂S, SO₂ and NO₂ fractions in gaseous CO₂ by using broadband absorption spectroscopy at 1 and 40 bar. The mole fractions of binary- and 3-component mixtures of H₂S, SO₂ and NO₂ in CO₂ with known fractions ranging from 35-250 ppm are successfully derived from the measured absorption spectra. The difference between the fitted and experimental mole fractions is less than 10% for all studied mixtures. The results successfully demonstrate that low fractions of H₂S, SO₂ and NO₂ in gaseous CO₂ can be accurately measured at pipeline conditions by using broad band absorption spectroscopy.

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1. Introduction

Increasingly stringent regulations regarding CO₂ emissions has called attention to capture the CO₂ from large point sources such as coal and gas fired power plants. The captured CO₂ will be transported and stored underground in, for example, empty gas fields or salt layers. Depending on the point source and the technology used, the captured CO₂ will contain other components such as, water, sulphur components (i.e. SO₂ and H₂S) and NO_x [1, 2] that may cause unwanted effects during transport and/or storage [3, 4]. Recent studies have indicated that these components can cause severe corrosion problems in the presence of water and affect the brine in underground storage [5, 6]. Moreover H₂S, SO₂ and NO₂ can cause health problems and therefore only limited amounts (ppm level) are allowed in CO₂ during transport. Therefore, it is of great importance to monitor real-time the absolute concentration of these components during CO₂ transport, which requires a robust and easy to operate measurement techniques that has a short response time.

In the past several techniques have been developed to measure H₂S, SO₂ and NO₂ at atmospheric pressures, such as electrochemical sensors [7-12]. One of the disadvantages of this technique is the relatively long response time and the need for frequent calibration. As an alternative, optical techniques such as Laser Induced Fluorescence (LIF) have high accuracy and a relatively fast response time [13]. Although H₂S, SO₂ and NO₂ absorbs strongly in the infrared (IR) spectral range [14], selective detection using an absorption technique such as Tunable Diode Laser Absorption Spectroscopy (TDLAS) [15] or Fourier Transform Infrared spectroscopy (FTIR) [16, 17] in this spectral range is difficult due to the interference from CO₂ and other impurities present in captured CO₂ in particular H₂O and CH₄.

Several studies reported measurements of H₂S, SO₂ and/or NO₂ using broadband absorption spectroscopy techniques in the ultraviolet region performed at atmospheric pressure [18-22]. In Ref. [18] the authors demonstrate that this relatively cheap and simple technique can be used to monitor real-time the SO₂ concentration in a boiler at a high sensitivity and fast response time. According to Ref. [21] the lower limit of detection for both SO₂ and NO₂ present in exhaust gases was 1 ppm by using broadband absorption in the UV-VIS[†] range having a fast response time (3.4s). To our knowledge no measurements of individual components or mixtures of H₂S, SO₂ and NO₂ have been performed at conditions relevant to CO₂ transport (up to 40 bar).

In this study we present a method for deriving the concentrations of H₂S, SO₂ and NO₂ present in CO₂ from absorption spectra measured at pressures ranging from 1-40 bar. The absorption measurements have been performed in the UV/VIS range; 220-500 nm. This range is selected because it is free of interference from other molecules present in captured CO₂. The method is based on the calculation of the theoretical absorption spectra by using absorption cross sections for H₂S, NO₂ and SO₂ reported in literature [23-25]. The concentrations of H₂S, NO₂ and SO₂ were determined by fitting the measured absorption spectrum. The method described in this paper allows determining low fractions (ppm level) of H₂S, NO₂ and/or SO₂ in CO₂ by using an easy and robust measurement technique with a fast response time.

2. Data reduction

In an absorption measurement, a signal, $I_m(\nu_0)$ measured by a detector that is attached to a spectrometer and tuned to the wavenumber ν_0 , can be written as;

$$I_m(\nu_0) = C \int_{-\infty}^{\infty} \varepsilon(\nu) I(\nu) G(\nu - \nu_0) d\nu + I_{D.C.}(\nu_0) \quad (1)$$

where $I(\nu)$ is the initial intensity of light at wavenumber ν received by the spectrometer, $I_{D.C.}(\nu_0)$ is the dark current at wavenumber ν_0 , C is the sensitivity of the photo detector, $\varepsilon(\nu)$ is the quantum efficiency of the photo detector, and G is the normalized instrument line function of the spectrometer which is defined as:

[†] UltraViolet-VISible

$$\int_{-\infty}^{+\infty} G(v - v_0) dv = 1 \quad (2)$$

Using the Beer-Lambert law the intensity $I(v)$ can be expressed as:

$$I(v) = I_0(v) e^{-\sum_i N_i \sigma_i(v) l + \alpha_{BG}(v) l} \quad (3)$$

Wherein $I_0(v)$ is the initial intensity of light at wavenumber v received by the spectrometer when the cell is filled with buffer gas, in this case CO_2 , $\sigma_i(v)$ is the absorption cross section of the species at wavenumber v , l is the absorption path length, N_i is the number density of the species, and α_{BG} is the absorption coefficient for species other than the species under investigation, which contribute to the background (BG) signal. The molecular number density N_i is related to the species mole fraction X_i using the ideal gas law,

$$N_i = X_i \frac{P}{k_B T} \quad (4)$$

where P is the pressure, T is the temperature, and k_B is the Boltzmann constant. Given that the bandwidth of the spectrometer is of several orders smaller than any change in $I_0(v)$, $\varepsilon(v)$ and $\alpha(v)l$ in the wavelength range studied we assume that these parameters can be regarded as constant when integrating over the instrumental bandwidth. By using the above mentioned assumption and substitution of equation (3) and (4) into equation (1), the following expression for the measured absorption signal $I_m(v_0)$ is acquired ;

$$I_m(v_0) = C \varepsilon(v_0) I_0(v_0) e^{-\alpha_{BG}(v_0) l} \int_{-\infty}^{+\infty} e^{-\sum_i \sigma_i X_i \frac{P}{k_B T}} G(v - v_0) dv + I_{D.C.}(v_0) \quad (5)$$

The signal detected by the spectrometer when the absorption path (cell) is filled with a buffer gas, $I_m^0(v_0)$ can be expressed as;

$$I_m^0(v_0) = C \varepsilon(v_0) I_0(v_0) e^{-\alpha_{BG}(v_0) l} + I_{D.C.}(v_0) \quad (6)$$

Combining equation (5) and (6) we can obtain the following expression for the absorbance $f(v)$:

$$f(v) = \ln \frac{I_m^0(v_0) - I_{D.C.}^0(v_0)}{I_m(v_0) - I_{D.C.}(v_0)} = -\ln \left(\int e^{-\sum_i \sigma_i X_i \frac{P}{k_B T}} G(v - v_0) dv \right) \quad (7)$$

According to expression (7) the mole fractions of the species under investigation (X_i) can be determined from the measured signals (I_m^0 , $I_{D.C.}^0$, I_m and $I_{D.C.}$) provided that the instrumental function of the spectrometer, $G(v - v_0)$, the experimental parameters (P , T , l), and the molecular parameters of the of the studied species, $\sigma_i(v)$ are known. For low concentrations of species, $X_i \ll 1$, the expression (7) can be further simplified,

$$f(v) \cong \ln \frac{I_m^0(v_0) - I_{D.C.}^0(v_0)}{I_m(v_0) - I_{D.C.}(v_0)} = X_i \frac{P}{k_B T} \sum_i \int \sigma_i(v) G(v - v_0) dv = X_i \frac{P}{k_B T} \sum_i \int \sigma_i(v) * G(v) dv \quad (8)$$

where symbol “*” denote the convolution procedure, as discussed below.

3. Experimental

Figure 1 presents the schematic of the experimental set-up for the broad band absorption measurements of NO_2 , SO_2 and H_2S in the UV region. A deuterium lamp with a power of 30W (Hamamatsu), was used as a broadband UV light source. The radiation of the lamp was focused by a convex lens to produce a parallel beam. The parallel beam passes through an absorption cell ($l=100$ cm) with two quartz windows and is subsequently focused into an optical

fiber (Ocean Optics OLFV-200-1100) that is connected to a spectrometer (HR2000CG). The spectrometer has a spectral range 200-1100nm, a resolution of 1 nm (FWHM). The samples are taken by using various integration times in order to obtain the highest signal-to-noise ratio and to prevent saturation of the detection system. The measurements are controlled by a PC using the spectrometer software.

Measurements at atmospheric pressure were performed in mixture of gases flowing through the absorption cell. To control the degree of mixing of the studied gas mixtures (H_2S , NO_2 , SO_2 in CO_2) the flow rates of all gases are were measured by calibrated mass flow meters. The flow ranges of the meters were selected to provide an accuracy of better than 5%. All test calibration gases used in this study have purity greater than 99.5%. After each experiment the sample cell was flushed for about 15 minutes.

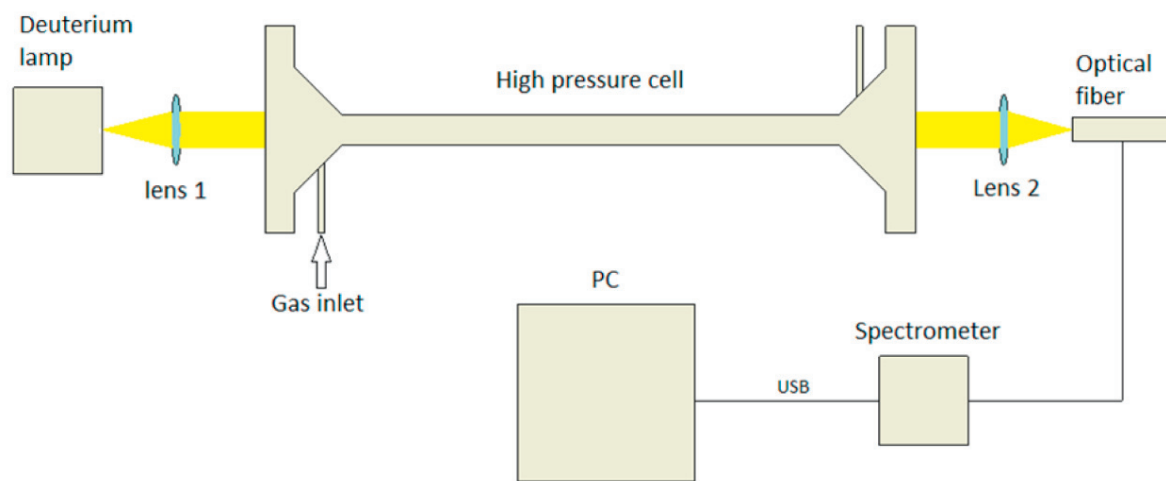


Figure 1: Schematic set-up

At pressures above 1 bar (up to 40 bar in this study) we used gas mixtures with known concentration of H_2S , SO_2 and/or NO_2 , which were manometrically prepared in the absorption cell itself. This means that during the preparation of the gas mixtures the cell is first filled with ~ 1 bar CO_2 . Subsequently, the components H_2S , NO_2 and/or SO_2 are added to the mixture by using calibration bottles with known concentrations H_2S , NO_2 and SO_2 in CO_2 . Next the cell is pressurized by adding pure CO_2 until the desired pressure is realized. The composition of the gas mixtures is calculated from the measured partial pressures of the individual pressures by using a GE Druck DPI 150 Precision Pressure Indicator with a precision of 0.01% full scale.

4. Experimental procedure

Prior to filling the absorption cell with SO_2 , NO_2 and/or H_2S in CO_2 as described above, we always first measure the intensity of the radiation after passing the absorption cell filled with pure CO_2 was measured, which gives us the $I_0(\nu)$ signal. Subsequently the cell is filled with a known concentration H_2S , NO_2 and/or SO_2 diluted with CO_2 and the intensity of the radiation that passed the cell is measured again, which gives us the transmitted signal $I(\nu)$. The dark current, $I_{D.C.}$ (signal observed without illumination) was measured after each reference and transmission measurement (see figure 2) and subtracted from the measured intensities, see equation 8. We remark that the $I_m(\nu_0)$ and $I_m^0(\nu_0)$ measurements are performed at identical pressure- and (room) temperature conditions.

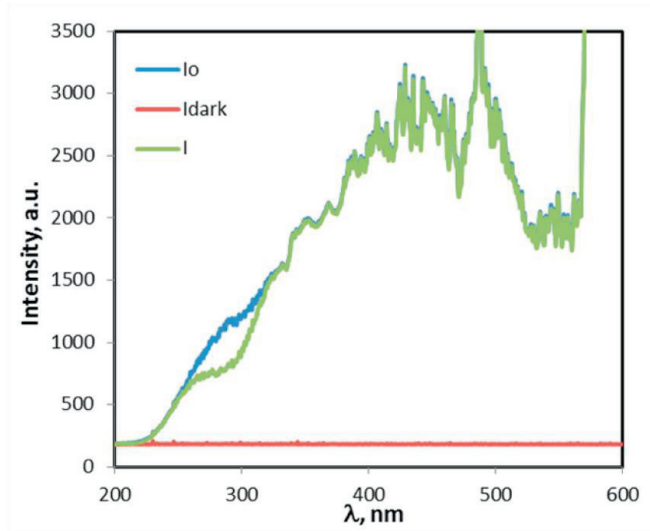


Figure 2: Transmission spectrum of 211 ppm SO₂ in CO₂ at 40 bar (blue), transmission spectrum of pure CO₂ at 40 bar (green) and dark current spectrum (red).

5. Fitting procedure for determining the H₂S, NO₂ and SO₂ concentration in CO₂

To determine the H₂S, NO₂ and SO₂ concentration in CO₂ a computer code was written that calculates the theoretical absorption spectrum by using equation (8). As an approximation of the instrumental function of the spectrometer the Lorentz function [26], described below is used in equation (8);

$$G(v - v_0) = \frac{2\Delta v_R}{\pi} \frac{1}{4(v - v_0)^2 + \Delta v_R^2} \quad (9)$$

where Δv_R is the Full Width at Half Maximum (FWHM) determined by the resolution of the spectrometer. By fitting the recorded spectrum of a Helium-Neon laser the line shape of the instrumental line profile of the used spectrometer is experimentally determined ($\Delta v_R = 1$ nm) which is used in the computer code. Furthermore the (high resolution) absorption cross sections for H₂S, NO₂ and SO₂ measured with N₂ or air as a buffer gas at atmospheric pressure reported in literature Refs. [23-25] are taken as input into the computer code together with the measured pressure P , temperature T and the absorption path l . Based on this input data and the experimentally measured absorption spectrum the computer code fits the mole fraction X_i using the Levenberg–Marquardt method [27, 28].

The absorption cross-section σ_i depends upon pressure P , see for example Ref. [29]. Unfortunately, information about the pressure dependence of the cross-section is unavailable. Formally, we can present the absorption cross section at arbitrary pressure $\sigma_{iP}(v)$ as a convolution of the absorption cross-section $G_P(v)$ and some unknown function $\sigma_{i0}(v) = \sigma_{i0}(v) * G_P$. Clearly, the function G_P is a delta-function at atmospheric pressure. With increasing pressure the width of this function should grow to smear spectral features. Thus our fitting function can be presented as,

$$f(v) = (\sigma_{i,0} * G_P) * G = \sigma_{i,0} * (G_P * G) = \sigma_{i,0} * G' \quad (10)$$

where we used association property of the convolution operation. It is reasonable to approximate G_p by the Lorentzian profile with the width $\Delta\nu_p$ depending upon pressure. This approximation substantially simplifies the fitting procedure. Because both functions G_{ip} and G are Lorentzian, their convolution G' is also a Lorentzian function, albeit with unknown width $\Delta\nu = \Delta\nu_R + \Delta\nu_p$, which can be determined by fitting procedure. Therefore, for pressures above 1 atm concentrations of the species and the width of the Lorentzian function ($\Delta\nu$) are also fitted.

6. Results and discussion

6.1. Atmospheric pressure spectra

Figures 3-5 show the NO_2/CO_2 , SO_2/CO_2 and $\text{H}_2\text{S}/\text{CO}_2$ absorption spectra measured at atmospheric pressure and room temperature. By fitting the measured absorption spectrum via the methodology described above the species concentrations of NO_2 , SO_2 and H_2S were determined, see Table 1. Here we note that the fractions given in Table 1, and mentioned in this paper, are converted to values at laboratory conditions ($T=294\text{K}$, $P=1.0$ bar). As shown in Table 1, the agreement between the experimental and fitted concentrations is better than 10% for studied gas mixtures.

Table 1: Experimental and fitted composition of NO_2 , SO_2 and H_2S in CO_2 measured at room temperature (294K) and pressures ranging from 1 - 40bar. The fractions are converted to values at standard conditions ($T=294\text{K}$, $P=1.0$ bar)

Single species								
No.	P, bar	Experimental fractions			Fitted fractions			Deviation ¹ , %
		NO_2 , ppm	SO_2 , ppm	H_2S , ppm	NO_2 , ppm	SO_2 , ppm	H_2S , ppm	
1	1	0	207	0	0	211	0	2.0
2	1	505	0	0	518	0	0	2.5
3	1	0	0	199	0	0	201	1.0
4	40	0	211	0	0	225	0	6.5
5	40	0	0	79.6	0	0	72	9.6
Mixed species								
6	1	158	121	90.2	152	123	90	3.9
7	1	136	89.2	111	123	94	113	9.7
8	1	120	142	97	120	153	97	7.6
9	1	178	83	97	179	79	105	7.8
10	1	148	107	100	145	110	102	2.8
11	1	240	182	34	224	191	35	4.3
12	1	101	149	102	105	157	106	5.4

¹For the ternary mixtures the largest deviation found between the experimental and fitted component fraction is presented

In Figures 3-5 the resulting fitted NO_2 , SO_2 and H_2S in CO_2 absorption spectra are shown as well. The NO_2 absorption spectrum (Figure 3) calculated by using the cross section given in Ref. [23] show excellent agreement with the measured absorption spectrum. Furthermore good agreement is found between the calculated NO_2 fraction (518 ppm) and the known NO_2 fraction (505 ppm) in the gas mixture.

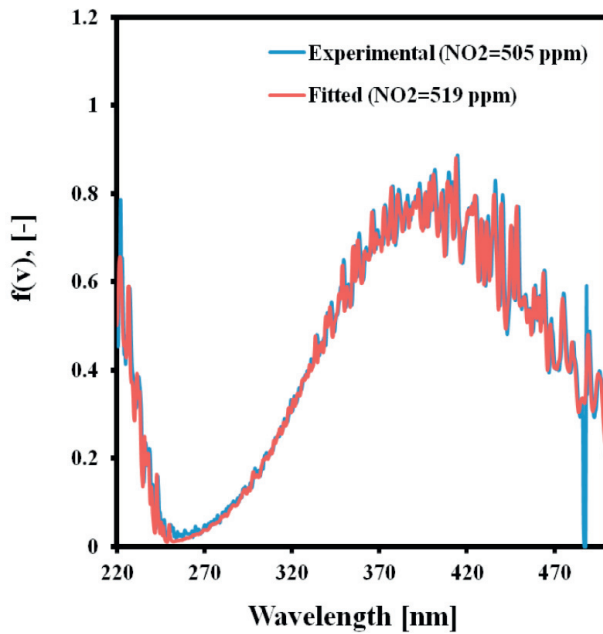


Figure 3: Measured and fitted NO₂ spectrum, measurement No. 2 (Table 1)

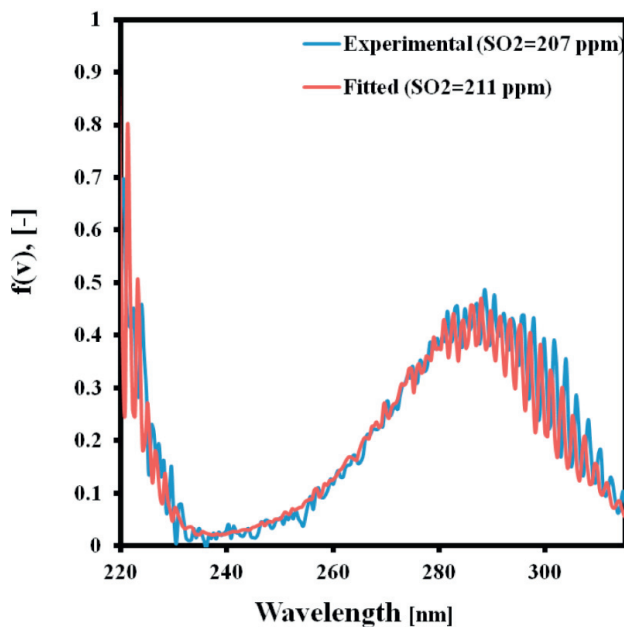


Figure 4: Measured and fitted SO₂ spectrum, measurement No. 1 (Table 1)

Figure 4 shows the SO₂ absorption spectrum measured in 207 ppm SO₂ in CO₂. The fitted absorption spectrum by using the cross section taken from Ref. [25] show good agreement at the left hand side of the figure (225-285 nm) while at the right hand side (285-305nm) the fitted absorption spectrum is slightly underpredicted. Nevertheless, the deviation between the fitted (211 ppm) and known SO₂ fraction (207ppm) is less than 5%.

Despite the noise observed in the measured spectrum a very good agreement is found between the measured and fitted and absorption spectrum for H_2S in CO_2 as presented in figure 5. The fitted absorption spectrum of H_2S is obtained by using the cross sections described in Ref. [24]. Furthermore the fitted H_2S fractions (201 ppm) are in excellent agreement with the known fraction in the calibration bottle (199 ppm).

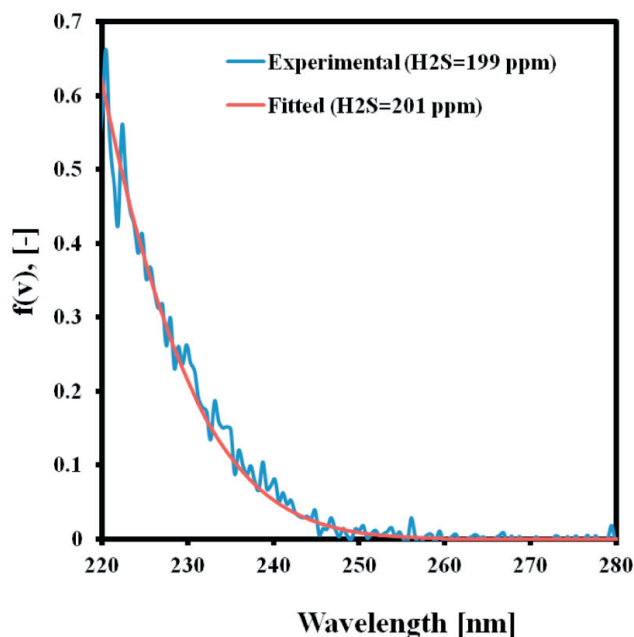


Figure 5: Measured and fitted H_2S spectrum, measurement No. 3 (Table 1)

6.2. Absorption spectra of ternary mixtures (H_2S , SO_2 and NO_2) in CO_2

As an example, Figure 6 shows the theoretical absorption spectrum of NO_2 , SO_2 and H_2S in CO_2 . The marked area shows the experimental spectral range, which is limited by the spectrometer (~ 220 nm). From Figure 6 it can be clearly seen that the absorption spectra of NO_2 , SO_2 and H_2S overlap each other within this spectral range, which complicates the determination of the mole fractions of the individual species for ternary mixtures.

As a test the computer code was used to determine the mole fractions of the individual species from the absorption spectra measured in ternary H_2S , NO_2 and SO_2 gas mixtures using known fractions (~ 35 - 250 ppm) in CO_2 . As an illustration Figure 7 presents the measured (red line) and fitted (blue line) absorption spectra of mixture no. 12 as given in Table 1. A very good agreement between the measured and fitted absorption spectra is observed in Figure 7. For all three components the fitted NO_2 , SO_2 and H_2S concentrations of the mixture are in excellent agreement with the experimental values. Table 1 presents the experimental and fitted mole fractions of all studied ternary (NO_2 , SO_2 and H_2S) mixtures in CO_2 . For all studied mixtures, having different ratios of NO_2 , SO_2 and H_2S , the difference between the experimental and fitted mole fractions is better than 10%.

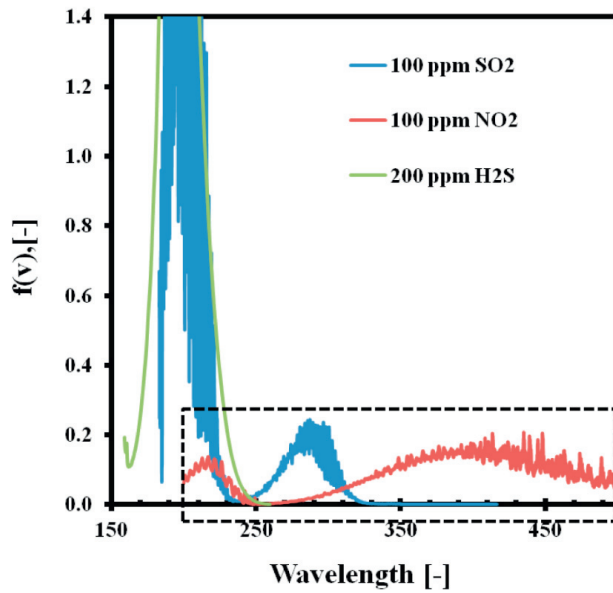


Figure 6: Theoretical absorption spectrum of NO_2 , SO_2 and H_2S .

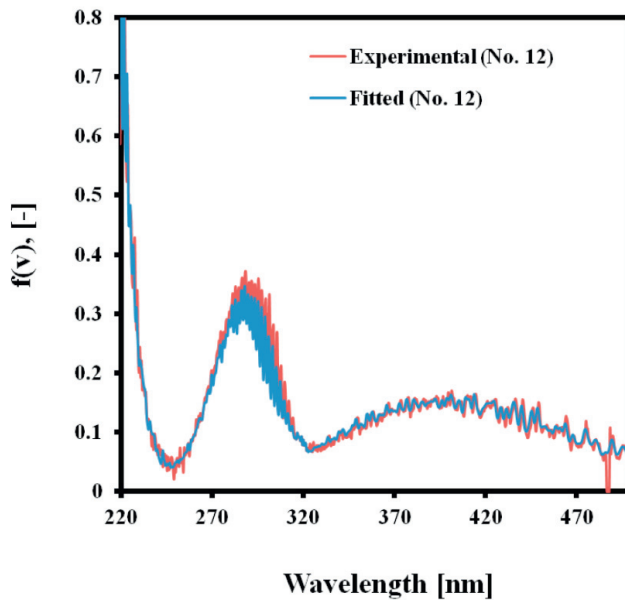


Figure 7: Measured and fitted absorption spectrum of NO_2 (101 ppm), SO_2 (149 ppm) and H_2S (102 ppm) in CO_2 (mixture no. 12, Table 1).

6.3. Absorption spectra of SO_2 and H_2S in CO_2 measured at 40 bar

To test if the above described broad band absorption methodology can be applied for determining the NO_2 , SO_2 and H_2S fractions at conditions relevant to CO_2 transport, we performed absorption measurements at a pressure up to 40 bar. As an example, Figure 8 presents the absorption spectrum of 211 ppm SO_2 measured at 2 bar and 40 bar. First, the cell was filled with a gas mixture containing SO_2 in CO_2 (no. 4, Table 1) at 2 bar and the absorption spectrum was recorded (green line). Subsequently the cell was further pressurized to 40 bar by adding pure CO_2 to the cell and the absorption spectrum (blue line) was recorded again. Clearly visible in Figure 8 are the fine structures of the SO_2 absorption spectrum in the region between ~ 280 -315nm for the measurements performed at 2 bar. However, as a result of pressure broadening the fine structures of the SO_2 absorption spectrum measured at 40 bar are substantially smoothed (blue line). The fitted SO_2 spectrum at 40 bar (red line in Figure 8) is obtained by using the cross sections determined at atmospheric pressure given in Ref. [25]. As mentioned above, the width of the Lorentzian function ($\Delta\nu$, see equation 9) is fitted to approximate the change in the cross sections due to pressure broadening [25]. The computed SO_2 spectrum shows a very good agreement with the measured SO_2 spectrum at 40 bar. Here we remark that the width of the Lorentzian function ($\Delta\nu$) increases by approximately one order due to pressure broadening when going from 1 to 40bar.

Additionally, absorption measurements are performed in $\text{H}_2\text{S}/\text{CO}_2$ and NO_2/CO_2 mixtures. The fitted and experimental concentrations for these measurements are shown in Table 1.

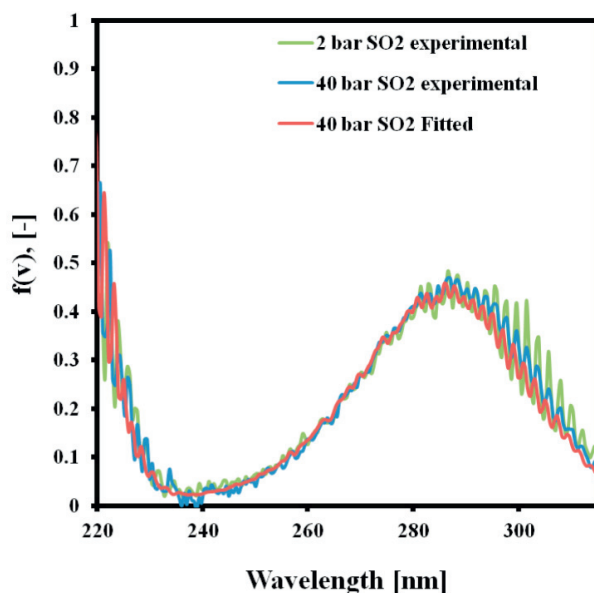


Figure 8: Measured absorption spectrum of 211 ppm SO_2 in CO_2 at 2 bar (green line) and at 40 bar (blue line), measurement number 4 (Table 1). The red line presents the fitted spectrum at 40 bar.

Following the same procedure as described above the H_2S spectra presented in Figure 9 were measured at 2- and 40 bar. As can be seen the noise at 40 bar is slightly increased in comparison to the absorption spectrum measured at 2 bar. Furthermore a small deviation of the fitted and experimental spectrum at 40 bar is observed. Despite of this deviation good agreement is found in the fitted H_2S fraction, see Table 1.

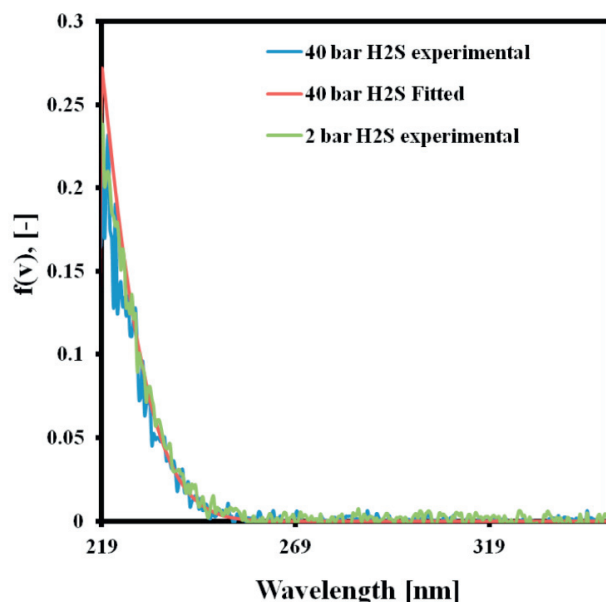


Figure 9: Measurement no. 5, experimental absorbance spectra of H₂S at 2 and 40 bar, along with the fitted spectrum.

Here we have to note that it was not possible to measure NO₂ under stationary conditions. During the experiments, it was surprisingly discovered that the concentration of NO₂ decreases in time, which may be due to accumulation or stickiness to the high pressure cell wall. Despite this result under stationary conditions we do not expect problems when measuring NO₂ concentrations at non stationary transport conditions. This was confirmed by experiments in this study at 1 bar in which the NO₂ was measured in a flowing gas stream consisting of NO₂/CO₂ (see for example Table 1 and Figure 3).

7. Conclusion

In this paper a methodology is described to measure quantitatively H₂S, SO₂ and NO₂ fractions in gaseous CO₂ by using broadband absorption spectroscopy in the UV/VIS range. To test this methodology absorption spectra in mixtures of H₂S, SO₂ and NO₂ in CO₂ with known mole fractions ranging from about 35-250 ppm have been measured in an absorption cell at flowing conditions (atmospheric conditions) and at stationary, non-flowing conditions (1-40bar). To derive the concentrations from the measured absorption spectra a method is developed that calculates the absorption spectra by using the absorption cross sections for H₂S, NO₂ and SO₂ reported in literature. By fitting the calculated and the experimentally determined absorption spectrum the concentrations of H₂S, NO₂ and SO₂ are determined in CO₂.

Comparison between the measured and fitted spectra obtained at atmospheric flowing conditions shows very good agreement over the entire range of measured component fractions. The difference between the fitted and experimental mole fractions of H₂S, SO₂ and NO₂ in CO₂ is less than 10%. Additionally, although the absorption spectra of H₂S, SO₂ and NO₂ gas mixtures studied show substantial interference the developed methodology can be successfully used to derive the individual species concentration within 10% accuracy.

Increasing the pressure from 1 to 40 bar, without changing the molecular concentration results in broadening of the fine structures of the measured SO₂/CO₂ absorption spectra. The calculations successfully take into account the observed pressure broadening.

The agreement between the fitted and experimental mole fractions for H₂S and SO₂ at 40 bar is better than 10% for the mixtures studied. Unfortunately, it was not possible to measure the NO₂ spectra under stationary conditions due to an observed decrease of the NO₂ fraction in time. However, as confirmed by the measurements at 1 bar it is expected that NO₂ can be successfully measured at 40 bar under flowing (transport) conditions.

The results of this study demonstrate that species concentrations of H₂S, SO₂ and NO₂ in CO₂ can be fast and accurately determined using broad band absorption spectroscopy.

Nomenclature

C	sensitivity of photo detector
l	absorption path length, cm
I	intensity of light, mV
$f(\nu)$	absorbance
G	Lorentz function, cm
k_B	Boltzmann constant, 1.3810^{-23} J/K
N_i	number density of species i, molecules/m ³
P	pressure, Pa
T	temperature, K
X_i	mole fraction
α	absorption coefficient, cm ⁻¹
ε	quantum efficiency of photo detector
$\Delta\nu$	FWHM of the Lorentzian profile, cm ⁻¹
ν	wavenumber, cm ⁻¹
σ_i	absorption cross section of species i, cm ² /molecule

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